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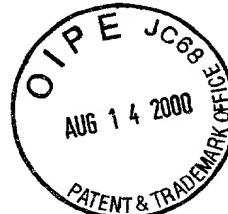


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August 14, 2000

BOX PCT

Honorable Commissioner of
Patents and Trademarks
Washington, D.C. 20231

Attorney Docket No. 225/49093

Re: Transmittal Letter to the United States
Designated/Elected Office (DO/EO/US)
Concerning a Filing Under 35 U.S.C. §371

International Application No.: PCT/EP99/00611
International Filing Date: January 30, 1999

Priority date claimed: February 13, 1998
Priority application number: 198 05 868.3

Inventorship: Tilmann HAUG
Kolja REBSTOCK
Christian SCHWARZ

Title: METHOD FOR PRODUCING A FIBER COMPOSITE

Enclosed herewith for entering the national stage in the United States is the above-referenced international application.

1. This is a FIRST submission of items concerning a filing under 35 U.S.C. §371.
2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371.
3. This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).

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INTERNATIONAL APPLN. NO.: PCT/EP99/00611
ATTORNEY DOCKET NO.: 225/49093

4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application as filed (35 U.S.C. §371(c) (2))
- a. _____ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. has been transmitted by the International Bureau. A copy of Form PCT/IB/308 is attached hereto.
 - c. _____ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. A translation of the International Application into English (35 U.S.C. §371(c) (2)).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c) (3))
- a. _____ are transmitted herewith (required only if not transmitted by the International Bureau)
 - b. _____ have been transmitted by the International Bureau
 - c. _____ have not been made; however, the time limit for making such amendments has NOT expired
 - d. _____ have not been made and will not be made
8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. §371(c) (3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. §371(c) (4)) is:
- [] Attached in the regular manner.
 NOT included, but deferred under P.L. 97-247.

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10. [] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5))
11. [] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [] An Assignment of the invention in favor of the following organization is enclosed for recordation. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST Preliminary Amendment.
[] A SECOND or SUBSEQUENT Preliminary Amendment.
14. [X] A substitute specification.
15. [] A change of power of attorney and/or address letter.
16. [X] Other items of information:
[] Form PCT/RO/101 Request (in English/in French)
[X] International Search Report
[] Small Entity Declaration Under 37 C.F.R. 1.27
[] _____ Sheets of Formal Drawings
[X] 3 Sheets of Informal Drawings
[] The content of the paper and computer readable copy of the attached Sequence Listing, submitted in accordance with 37 CFR §1.821(c) and (e), respectively, are the same.
[X] Kindly appoint as associate attorneys (if not already a principal attorney) or agents:
Herbert I. Cantor, Reg. No. 24,392; James F. McKeown, Reg. No. 25,406; Donald D. Evenson, Reg. No. 26,160; Joseph D. Evans, Reg. No. 26,269; Gary R. Edwards, Reg. No. 31,824; and Jeffrey D. Sanok, Reg. No. 32,169

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INTERNATIONAL APPLN. NO.: PCT/EP99/00611
ATTORNEY DOCKET NO.: 225/49093

[X] The total amount due for the filing fee in this case
is:

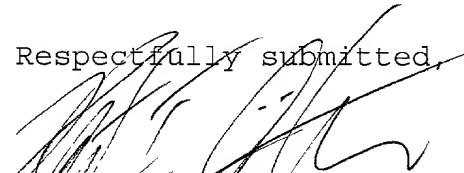
[] Based on Small Entity Status

Total Number of Claims: 31
Total Independent Claims: 1

Basic filing fee, \$840/\$420.	\$ <u>840.00</u>
Independent Claims above 3, \$78/\$39 ea.. . . .	\$ _____
Total claims in excess of 20, \$18/\$9 ea. . . .	\$ <u>198.00</u>
Multiple dependency penalty, \$260/\$130	\$ <u>260.00</u>
Declaration surcharge, \$130/65	\$ _____
English translation surcharge, \$130	\$ _____
TOTAL FILING FEE DUE \$ <u>1,298.00</u>	

Please forward all communications regarding this
application to the undersigned at the letterhead address.

Respectfully submitted,


Herbert I. Cantor
Reg. No. 24,392

HIC/tcv

THE COMMISSIONER IS AUTHORIZED TO CHARGE ANY FEES
WHICH MAY BE REQUIRED OR CREDIT ANY OVERPAYMENT TO
DEPOSIT ACCOUNT NO. 05-1323. THIS FORM IS FILED IN
DUPLICATE.

THIS IS A GENERAL AUTHORIZATION EXCLUDING ONLY
PAYMENT OF THE ISSUE FEE.

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Attorney Docket: 225/49093
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: TILMANN HAUG ET AL.

Serial No.: TO BE ASSIGNED

International Application No.: PCT/EP99/00611

Filed: CONCURRENT HEREWITH

International Filing Date: January 30, 1999

Title: METHOD FOR PRODUCING A FIBER COMPOSITE

PRELIMINARY AMENDMENT

Box PCT

Commissioner for Patents
Washington, D.C. 20231

Sir:

Please enter the following amendments to the claims and abstract of the disclosure, prior to calculation of the filing fee and the examination of the application during the U.S. National Phase.

IN THE CLAIMS

Please amend Claims 1-17 as follows:

--1. (Amended) A process [Process] for producing a [fibre] fiber composite material [containing fibres] comprising filling (A) fibers with a high hot strength, based on at least one of carbon, silicon, boron [and/or] and nitrogen, which are reaction-bonded to a silicon-based matrix, [a] (B) a plurality of pressing

[compound being] compounds produced from [fibres] fibers of different qualities and/or in different proportions, and (C) a binder [and, if appropriate, filler and/or additives, which is then pressed in] into a press [mould] mold and then pressing the same to form a green body, [characterized in that various pressing compounds are produced, which contain fibres of different qualities and/or in different proportions, and] wherein the press [mould] mold is filled with the [various] pressing compounds in a plurality of successive steps.

2. (Amended) A process [Process] according to Claim 1, wherein the press [mould] mold is filled without preforming.

3. (Amended) A process [Process] according to [one of the preceding claims, characterized in that fibres which] Claim 1, wherein said fibers have been coated with a layer of [pyrolysable] a pyrolyzable binder [are used].

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4. (Amended) A process [Process] according to [one of the preceding claims, characterized in that fibres which] Claim 1, wherein said fibers have been coated with a layer of pyrolytic carbon and with a layer of [pyrolysable] a pyrolyzable binder [are used].

5. (Amended) A process [Process] according to [one of the preceding claims, characterized in that] Claim 1, wherein differently coated [fibres] fibers are used for the various pressing compounds.

6. (Amended) A process [Process] according to Claim 5, [characterized in that] comprising filling the press mold [mould is filled] with the differently coated [fibres] fibers in such a manner that a green body is formed[,] from which it is possible to obtain a [fibre] fiber composite material with a substantially graphite core and a substantially ceramic surface.

7. (Amended) A process [Process] according to Claim 6, [characterized in that fibres] wherein fibers with a pronounced coating are used for the substantially graphite core and [fibres] fibers with a thin coating and/or [fibres] fibers without a coating are used for the substantially ceramic surface.

8. (Amended) A process [Process] according to Claim 6, [characterized in that fibres] wherein fibers with a coating which is relatively unreactive with respect to the matrix are used for the substantially graphite core and [fibres] fibers with

a coating which is more reactive with respect to the matrix are used for the substantially ceramic surface.

9. (Amended) A process [Process] according to [one of the preceding claims, characterized in that] Claim 1, wherein substantially short [fibres] fibers or short [fibre] fiber bundles are used to produce the pressing compounds.

10. (Amended) A process [Process] according to [one of the preceding claims, characterized in that fibres] Claim 1, wherein fibers of different lengths are used for the various pressing compounds.

11. (Amended) A process [Process] according to [one of the preceding claims, characterized in that fibres] Claim 1, wherein fibers made from different materials are used for the various pressing compounds.

12. (Amended) A process [Process] according to [one of the preceding claims, characterized in that] Claim 1, wherein [to produce the pressing compounds] the individual components are processed into granules [, in particular by being pelletized] to

produce the pressing compounds, and the granules are dried and pressed to form the green body.

13. (Amended) A process [Process] according to Claim 12, [characterized in that] wherein the granules are pressed by dry or hot extrusion.

14. (Amended) A process [Process] according to [one of Claims] Claim 1 [to 11, characterized in that to produce the pressing compound], wherein the individual components are mixed in a kneader to produce the pressing compound and the mixture is pressed to form a green body.

15. (Amended) A process [Process] according to [one of the preceding claims, characterized in that] Claim 1, wherein a heat-curable binder is added to the pressing compound, and the pressed green body is cured by heating.

16. (Amended) [Fibre] A fiber composite material containing [fibres] fibers with a high hot strength, based on carbon, silicon, boron and/or nitrogen, which are reaction-bonded to a silicon-based matrix, [characterized in that it can be

produced using] made by the process [according to] of one of Claims 1 to 15.

17. (Amended) [Fibre] A fiber composite material according to Claim [16, characterized in that it contains fibres] 1, containing fibers with a layer of carbon and/or pyrolytic carbon.--

Please cancel Claims 18-20 without prejudice or disclaimer.

Please amend Claim 21 as follows:

--21. (Amended) [Fibre] A fiber composite material [according to Claim 19, characterized in that] made by the process of Claim 6, wherein the substantially graphite core contains few or no [fibres] fibers which are reaction-bonded to the matrix, and the substantially ceramic surface contains predominantly or exclusively [fibres] fibers which are reaction-bonded to the matrix.--

Please cancel Claims 22-24 without prejudice or disclaimer.

Serial No. TO BE ASSIGNED

Please insert the following new claim:

--25. A process according to Claim 1, wherein the individual components are processed into granules by being pelletized.--

IN THE ABSTRACT

Please cancel the abstract in its entirety and insert the abstract submitted herewith on a separate page.

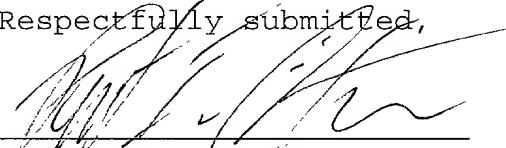
REMARKS

Entry of the amendments to the claims and abstract of the disclosure prior to examination of the application in the U.S. National Phase are respectfully requested.

Serial No. TO BE ASSIGNED

If there are any questions regarding this Preliminary Amendment or this application in general, a telephone call to the undersigned would be appreciated since this should expedite the prosecution of the application for all concerned.

Respectfully submitted,


Herbert I. Cantor
Registration No. 24,392

August 14, 2000

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ABSTRACT OF THE DISCLOSURE

The invention relates to a process for producing a fiber composite material containing fibers with a high hot strength, in particular based on carbon, silicon, boron and/or nitrogen, a pressing compound being produced from fibers, a binder and, if appropriate, fillers and/or additives, which is then pressed in a press mold to form a green body. Various pressing compounds are produced, which contain fibers of different qualities and/or in different proportions, and the press mold is filled with the various pressing compounds in a number of successive steps. The invention also relates to a fiber composite material of this nature.

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SUBSTITUTE SPECIFICATION

PROCESS FOR PRODUCING A FIBRE COMPOSITE MATERIAL

This invention relates to a process for producing a fiber composite material and to a fiber composite material containing fibers with a high hot strength, a pressing compound produced from fibers, a binder and, if appropriate, fillers and/or additives. More particularly, the fibers are based on carbon, silicon, boron, and/or nitrogen. The mass is then pressed in a press mold to form a green body.

A process of the generic type and a ceramic composite material of the generic type are described in German Patent Application 197 11 829.1, which is not a prior publication. The reinforcing fibers which are known from this document are fibers with a high hot strength which are present in the form of short fiber bundles. The fiber bundles are impregnated with a binder which is suitable for pyrolysis. For this purpose, the fiber bundles are dipped into the binder. The binder is then solidified. Consequently, the fiber bundles are held together and mechanically reinforced. The fiber bundles are mixed with further binders and fillers and the mixture is hot-pressed to form a CRP body or "green body", which is then pyrolyzed in vacuo or under an inert gas to form a shaped body with a carbon matrix (C/C body). In the process, the fiber coating is also converted so that the fiber bundles are then coated with a layer of carbon. The shaped body is then infiltrated with molten silicon. The result is a C/SiC fiber composite material in which the fiber bundles are embedded in a matrix based on SiC. The short fiber bundles are embedded in the matrix in a randomly distributed form, with the individual filaments being substantially maintained. The carbon coating has reacted with the matrix material. As a result, the fiber bundles are protected from the

aggressive attack from the molten silicon. This fiber composite ceramic exhibits very good tribological properties and, furthermore, is relatively inexpensive and easy to produce. It is suitable in particular for
5 the production of brake discs and/or brake linings.

However, this material is unable to withstand particularly high mechanical loads, such as for example those which are generated by high vehicle masses or extreme speeds, since it is too brittle and
10 insufficiently tolerant to damage to do so.

Various solutions have already been proposed in order to circumvent this problem. German Utility Model 296 10 498 describes a vehicle brake disc or vehicle clutch disc made from C-C/SiC composite material in
15 which the disc has an SiC coating. Therefore, the outer region of the disc is made from ceramic material and provides very good frictional characteristics, while the core is a carbon body which, due to its pseudoductility, has high tolerance to damage.
20 However, bodies that are coated in this way are complex and therefore expensive to produce. For this reason, they are only used for special applications, for example in motor racing.

European Patent Application EP 0 564 245 likewise
25 describes a multilayer material which, however, has to be provided with a protective layer in order to prevent silicon from penetrating into relatively deep regions. This too is a highly complex and expensive process.

Therefore, the object of the invention is to provide a fiber composite material of the above type which offers an even higher strength and improved pseudoductility of the component. A further object of
30

the invention is to provide a process for producing this material, making the material simple and inexpensive to produce and therefore suitable for series production.

5 The solution consists in a process for producing a fiber composite material containing fibers with a high hot strength, based on carbon, silicon, boron and/or nitrogen, which are reaction-bonded to a silicon-based matrix, a pressing compound being produced from fibers,
10 binder and, if appropriate, filler and/or additives, which is then pressed in a press mold to form a green body, wherein various pressing compounds are produced, which contain fibers of different qualities and/or in different proportions, and the press mold is filled
15 with the various pressing compounds in a plurality of successive steps and in a fiber composite material containing fibers made by the process. The fibers preferably have a layer of carbon and/or pyrolytic carbon.

20 The process according to the invention is distinguished by the fact that, to produce the green body, the press is successively filled with the various pressing compounds, the inner pressing compound comprising fibers of a core which is tolerant to damage, and the outermost pressing compound comprising
25 fibers in a ceramicized frictional coating.

30 The material according to the invention is therefore a gradient material, the advantage of which lies in the extremely simple production process according to the invention.

According to the invention, during the production of the green body, the pressing compounds, during

filling, are to be layered in the press mold in such a way that in the final component the frictional layer which has a high wear resistance and is largely ceramicized merges continually into a core which is tolerant to damage. In this way, the high wear resistance is combined with very good mechanical characteristics.

Therefore, if the mechanical loads on the component are extremely high, it is possible to further increase strength and extension characteristics, as can be demonstrated for example in the 3-point bending test. Under particularly high mechanical loads, such as for example those caused by high vehicle masses or extreme speeds, it is possible to adapt known processes for the low-cost production of fiber-reinforced composite ceramic in such a way that the material or the component offers a high strength and a very good resistance to wear on the outside, combined with a significantly increased pseudoductility on the inside.

The advantage of the process according to the invention is that there is no need to join layers with different properties using complex joining processes. In this case, the gradient is produced solely by the way in which the mold is filled. Due to the process used, the individual layers do not have any defined interlayers.

The filling heights required can be determined according to the particular application using tests on the compressibility of the various pressing compounds at constant pressure.

A highly ceramicized frictional layer on the component surface, for example the brake disc surface, is obtained by providing the fibers which have been processed in the pressing compound with coatings which make it possible for not only carbon-containing fillers and pyrolyzed binders but also carbon fibers to be partially converted by the molten silicon to form silicon carbide. This is achieved by applying known coatings in a suitably small thickness or using more reactive carbon-containing coatings.

As a result, the fibers which have been provided with a corresponding thin coating are relatively soft during processing to form the pressing compound. After mixing and pressing, they exhibit a high degree of interlacing. This means there are few, if any, spaces between them in which, for example, silicon can accumulate and therefore remain as unreacted residual silicon following the infiltration with liquid silicon. Furthermore, the fibers are reaction-bonded to the matrix. The result is a high proportion of ceramic fibers. The frictional layer formed therefore has a high strength with an excellent tolerance to damage and is characterized by a high resistance to wear. A brake disc produced using this process has, for example, a high coefficient of friction with suitably adapted linings.

A layer of pyrolytic carbon (PyC) is applied to at least some of the reinforcement fibers used. Only then is a simple dip coating in accordance with the known process carried out.

These preferred reinforcement fibers are therefore each individually coated with two additional layers. The bottom layer, which is applied direct to the fiber,

is made from pyrolytic carbon. A dip-coating which is known per se comprising a pyrolyzable binder is applied to this layer. During the infiltration of the porous shaped body with liquid silicon, the layer of carbon resulting from the resin coating acts as a "sacrificial layer". The liquid silicon reacts with this outer layer to form silicon carbide. This forms a diffusion barrier to the liquid silicon, which therefore cannot penetrate further into the fiber. The deeper layer of pyrolytic carbon and the reinforcement fibers in the core are not attacked.

The fibers which have been treated in this way are distinguished by a particularly high strength. The additional layer of pyrolytic carbon also produces optimum bonding of the reinforcement fibers to the matrix. They have a crack-diverting action and can slide in the longitudinal direction, resulting in the good results of the strength and 3-point bending tests. fiber-pullout effects are possible.

By using these reinforcement fibers during the production of the fiber composite material according to the invention, even in small proportions of the total fiber volume, it is possible to significantly increase the strength and extension figures, as can be demonstrated, for example, using the 3-point bending test. They do not impair the other parameters.

By coating the PyC fibers with a resin solution, it is possible to use these fibers even for silicized materials.

The process for producing these reinforcement fibers is distinguished by the fact that carbon fibers are firstly coated with pyrolytic carbon. This term is

understood to mean both pyrolyzed dip coatings, such as for example pitch, and layers deposited from the vapor phase. The fibers are then provided with pyrolyzable plastic material.

5 The coating with pyrolytic carbon may, on the one hand, be carried out by dip coating, for example by dipping into a pitch bath. This process is suitable in particular for long fibers. Alternatively, a CVD coating, for example using methane in a reactor, may be
10 applied to the fibers. This process is eminently suitable for both long fibers and short fibers.

15 The use of pitch has the advantage that the pyrolytic carbon layer formed is crystalline carbon which reacts with liquid silicon significantly more slowly than a layer of amorphous carbon, as is formed, for example, when a phenolic resin is used. As a result, the diffusion barrier for the amorphous carbon is strengthened further.

20 Long fibers are preferably cut after the coating and before they are processed to form a green body.

25 It is possible to use treated individual fibers or fiber bundles. The fiber bundles preferably comprise approximately 1000 to 14,000 individual fibers, with mean diameters of approximately 5 to 10 μm and a length of approximately 1 to 30 mm. In this way, it is also possible to use commercially available fiber bundles, allowing inexpensive production.

30 For the gradient material according to the invention, this means that the pressing compounds which have been layered successively into the press mold contain reinforcement fibers in which the quality of

the fiber coating increases from the outside inwards.
For example, in the core of a subsequent brake disc
PyC-coated carbon fibers are used, so that the entire
component is made tolerant to damage. Further filling
5 is with pressing compounds which contain fibers of
decreasing coating quality, until ultimately fibers
with only a slight coating – and in extreme cases even
uncoated fibers – are used for the frictional layer.
The outermost layer, which then serves as the actual
10 frictional layer, may therefore comprise predominantly
or even entirely silicon carbide, since the slightly
coated or even uncoated fibers are predominantly or
completely converted into silicon carbide during the
liquid silicization.

Furthermore, it is possible to achieve the
gradient in mechanical and tribological properties not
only by using the fiber coating but also by varying
both the fiber quality and the fiber length.

The use of short fibers has the further advantage
that the filling and pressing operation also orients
fibers perpendicular to the pressing plane, thus
ensuring a continuous transition of the properties.

All customary reinforcement fibers can be used to
produce the material according to the invention.
25 Carbon fibers are preferred. However, other fibers with
high hot strength, such as silicon carbide fibers or
fibers based on Si/C/B/N, are suitable in principle.
Furthermore, glass fibers or metal fibers, for example
fibers based on titanium, are suitable. Aramid fibers
30 are also eminently suitable.

These different variables, in combination, make it possible to produce a defined change in the materials' properties over the thickness of the disc.

Exemplary embodiments of the present invention are described in more detail below with reference to the appended drawings, in which:

Figure 1 is a diagrammatic depiction of a cross section through a PyC-coated carbon fiber;

Figure 2 is a diagrammatic cross section through a gradient material according to the invention;

Figure 3 is a picture of a brake disc which has been produced using the process according to the invention, in the CRP state (green body); and

Figures 4 and 5 are microsections through the gradient structure of the brake disc shown in Figure 3.

The reinforcement fiber 1 shown in Figure 1 has an inner core 2 made from a carbon fiber. This core 2 is provided with a coating 3 of pyrolytic carbon. The coating 3 is preferably approximately 100-300 nm thick. An outer layer 4 made from a pyrolyzable binder is preferably applied to the coating 3. The layer 4 is preferably approximately 200-800 nm thick. This binder is, for example, a pyrolyzable resin or resin mixture, preferably selected from the group of phenolic resins. The layer 4 is converted into carbon during the subsequent pyrolysis, and this carbon in turn reacts to form silicon carbide during the infiltration with liquid silicon. The inner region of the reinforcement fiber 1, namely the coating 3 of pyrolytic carbon and the core 2 of the reinforcement fiber 1, which is

enclosed by the coating 3, are not affected by the liquid silicon.

These fibers can be produced in various ways. One possible process is eminently suitable for coating long fibers. The long fibers are firstly dipped into a pitch bath and are then dried in a drying station. The fibers which have been coated in this way are finally dipped into a bath containing a pyrolyzable phenolic resin. After they have passed through a further drying station, the long fibers are ready for use and may, for example be cut to the desired length.

A further possible process is suitable both for coating short fibers and for coating long fibers. The fibers are firstly subjected to a CVD coating, for example using methane, and then to a dip coating in a bath containing pyrolyzable phenolic resin.

The production process for the material according to the invention is known per se and is described, for example, in German Patent Application 197 11 829.1.

The mixture for producing the green bodies comprises fibers or fiber bundles, a pyrolyzable binder, e.g. a phenolic resin, and, if appropriate, carbon-containing fillers, such as graphite or soot, as well as further fillers, such as silicon, carbides, nitrides or borides, preferably silicon carbide, titanium carbide or titanium boride in powder form. Examples of further preferred fillers for influencing the pyrolysis kinetics, in particular for accelerating the pyrolysis, are polyvinyl alcohol or methylcellulose. Furthermore, additions of iron, chromium, titanium, molybdenum, nickel or aluminum may

be added to the mixture. These additions improve the behavior of the liquid silicon during the infiltration.

The baths may also already contain fillers, such as for example graphite.

5 The carbon-containing fillers assist with cohesion during production and subsequent pyrolysis of the green body and accelerate the pyrolysis. The further fillers are used to adjust the wear resistance of the subsequent composite ceramic.

10 The green body may be produced by dry or hot extrusion of granules. The granules may be obtained by pelletizing the components listed above. Following their production, the granules are dried and pressed to form a green body. It is possible to produce the green body near net shape. Since there is little shrinkage during the pyrolysis and infiltration with liquid silicon, remachining costs are low.

15 However, the mixture described above may also be mixed with heat-curable binders in a kneader, pressed in a mold and heat-cured to form a green body. In this case, the green body or the porous shaped body resulting from the pyrolysis of the green body may be machined further to a desired shape.

20 The porosity of the shaped body can be set by selecting the additives and the amount thereof.

25 Exemplary Embodiment 1

Three different pressing compounds were produced from short fibers SCF6 with a length of 6 mm and short

fibers SCF3 with a length of 3 mm, produced by SGL,
phenolic resin, titanium carbide and graphite filler.

Pressing compound 1 contained 3 mm fibers with
exclusively a commercially available epoxy resin coat.
5 Pressing compound 2 contained 6 mm fibers which were
coated by impregnation in a pitch solution (Carbores,
produced by Rüttgers) and subsequent drying. The
coated fibers were then impregnated by immersion in a
highly dilute phenolic resin solution and subsequent
10 drying in a circulating-air cabinet at 130°C. Pressing
compound 3 contained a mixture of 3 mm and 6 mm fibers
in a ratio of 1:2, which, as described above, were
firstly dipped into the pitch solution referred to
above and then into a concentrated phenolic resin
15 solution. This was again followed by a drying and
curing step.

The three pressing compounds were produced from
the different coated fibers using a known process. To
do this, untreated or treated fibers were mixed with
phenolic resin, titanium carbide and graphite as filler
20 in a mixing kneader to form a pressing compound. The
fibers formed 38% by volume.

These pressing compounds were used to produce a
brake disc. To do this, the near net shape mold of a
25 hot press was filled. The filling took place in five
steps without preforming. Firstly, the mold was filled
with pressing compound 1; the height of the layer was
approx. 13 mm. This was followed by a second layer of
pressing compound 2, to a height of approximately 10
mm, a third layer of pressing compound 3, to a height
30 of approximately 20 mm, a fourth layer of pressing
compound 2, to a height of approximately 10 mm, and a
fifth and final layer of pressing compound 1, to a

height of approximately 13 mm. These layers were pressed under a pressure of approximately 80 bar. The result was a disc with a thickness of approximately 25 mm.

5 This pressing compound was cured at approximately 150°C to form a dimensionally stable CRP disc, as shown in Figure 3. Pyrolysis took place at 800°C in a pyrolysis furnace under inert gas. The subsequent infiltration with liquid silicon was carried out in vacuo at approximately 1600°C, using molten silicon. 10 The resultant C/SiC body was cooled to room temperature.

15 The resultant brake disc was tested with brake linings made from the same material with a lower silicon content. The coefficients of friction were very good at 0.55 - 0.6.

20 The flexural strengths were determined separately for the individual layers. The 3-point bending strength of the material derived from the pressing compound 1 was approximately 170 MPa with an extension of 0.12%. The 3-point bending strength of the material derived from pressing compound 2 was approximately 91 MPa with an extension of 0.09%. Finally, the 3-point bending strength of the material derived from pressing compound 3 was approximately 67 MPa with an extension of 0.21%.

25 Exemplary Embodiment 2

30 The same proportions of short fibers SCF3 with a length of 3 mm and short fibers SCF6 with a length of 6 mm produced by SGL and T 800/6K fibers produced by Toray with a length of 24 mm were used. The 3 mm

fibers and 6 mm fibers were firstly provided, as described above, with a layer of pyrolytic carbon and then with a layer of phenolic resin. The 24 mm fibers had a layer of pyrolytic carbon (PyC) applied using a CVD process by means of methane, and a resin coating which was applied by dipping.

The fibers which had been treated in this way were processed to form a pressing compound as described above. The fibers which had been coated according to the invention again constituted 38%. These fibers were mixed with phenolic resin, titanium carbide and graphite as filler, in a mixing kneader, to form a pressing compound.

Three different pressing compounds were produced, as described above, with pressing compounds 1 and 2 having the compositions described above and pressing compound 3 containing a mixture of 24 mm fibers and 6 mm fibers, in a ratio of 1:2.

The near net shape mold of the hot press was filled in five steps without preforming, as described above, the filling height of the layers of the pressing compound 1 being in each case 10 mm, and the height of the layers of the pressing compound 2 in each case being approximately 12 mm. The layered arrangement was pressed at 80 bar. The result was a disc with a thickness of approx. 25 mm.

The pressing compound was cured at approximately 150°C to form a dimensionally stable CRP disc. Pyrolysis took place at 800°C in a pyrolysis furnace under inert gas. The subsequent silicization was carried out in vacuo at approximately 1600°C using

molten silicon. The resultant C/SiC body was cooled to room temperature.

The coefficients of friction, which were measured as described above, were once again 0.55 - 0.6. The 3-point bending strength of the material derived from pressing compound 2 (thick resin coating) was approx. 67 MPa with an extension of 0.21%. The 3-point bending strength of material derived from pressing compound 3 (PyC-resin coating) was approximately 107 MPa with an extension of 0.42%.

Figure 2 diagrammatically depicts a cross section through a brake disc 10 produced using this process. The central opening in the brake disc is denoted by 11, and the disc material itself is denoted by 12. The brake disc 10 comprises the gradient material 12 according to the invention. The outermost regions 13a, 13b at the surface of the brake disc 10 form the frictional surfaces. They comprise wear-resistant, high-strength ceramic substance. The central region 15 in the interior of the brake disc 10 forms a core which is tolerant to damage. It comprises a carbon-containing material with relatively unpronounced ceramic properties, lacking in particular the brittleness which is typical of ceramic materials. The regions 14a and 14b form intermediate regions, the material of which is not as strongly ceramic as that of the outer regions 13a, 13b but also not as carbonaceous as the material of the central region 15.

The phase boundaries 16a, b, c, and d between the individual regions 13a, b, 14a, b, 15 are not sharply emphasized, but rather are more gradual. Preferably, they merge into one another. The process according to the invention ensures a gradual transition and

therefore good cohesion between the regions.
Additional joining processes are not required.

5 Figure 3 shows a brake disc which has been produced in accordance with Exemplary Embodiment 1 in the CRP state i.e. after pressing but before pyrolysis of the green body and before infiltration with liquid silicon.

10 Figures 4 and 5 show microsections through the gradient structure of the porous shaped body shown in Figures 2 and 3. The various layers which merge seamlessly into one another can be seen clearly.

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MARKED-UP
SUBSTITUTE SPECIFICATION

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PROCESS FOR PRODUCING A FIBRE COMPOSITE MATERIAL

The This invention relates to a process for producing a fibre fiber composite material according the preamble of Claim 1 and to a fibre fiber composite material according the preamble of Claim 16 or 17 containing fibers with a high hot strength, a pressing compound produced from fibers, a binder and, if appropriate, fillers and/or additives. More particularly, the fibers are based on carbon, silicon, boron, and/or nitrogen. The mass is then pressed in a press mold to form a green body.

A process of the generic type and a ceramic composite material of the generic type are described in German Patent Application 197 11 829.1, which is not a prior publication. The reinforcing fibres fibers which are known from this document are fibres fibers with a high hot strength which are present in the form of short fibre fiber bundles. The fibre fiber bundles are impregnated with a binder which is suitable for pyrolysis. For this purpose, the fibre fiber bundles are dipped into the binder. The binder is then solidified. Consequently, the fibre fiber bundles are held together and mechanically reinforced. The fibre fiber bundles are mixed with further binders and fillers and the mixture is hot-pressed to form a CRP body or "green body", which is then pyrolysed pyrolyzed in vacuo or under an inert gas to form a shaped body with a carbon matrix (C/C body). In the process, the fibre fiber coating is also converted so that the fibre fiber bundles are then coated with a layer of carbon. The shaped body is then infiltrated with molten

silicon. The result is a C/SiC fibre fiber composite material in which the fibre fiber bundles are embedded in a matrix based on SiC. The short fibre fiber bundles are embedded in the matrix in a randomly distributed form, with the individual filaments being substantially maintained. The carbon coating has reacted with the matrix material. As a result, the fibre fiber bundles are protected from the aggressive attack from the molten silicon. This fibre fiber composite ceramic exhibits very good tribological properties and, furthermore, is relatively inexpensive and easy to produce. It is suitable in particular for the production of brake discs and/or brake linings.

However, this material is unable to withstand particularly high mechanical loads, such as for example those which are generated by high vehicle masses or extreme speeds, since it is too brittle and insufficiently tolerant to damage to do so.

Various solutions have already been proposed in order to circumvent this problem. German Utility Model 296 10 498 describes a vehicle brake disc or vehicle clutch disc made from C-C/SiC composite material in which the disc has an SiC coating. Therefore, the outer region of the disc is made from ceramic material and provides very good frictional characteristics, while the core is a carbon body which, due to its pseudoductility, has high tolerance to damage. However, bodies that are coated in this way are complex and therefore expensive to produce. For this reason, they are only used for special applications, for example in motor racing.

European Patent Application EP 0 564 245 likewise describes a multilayer material which, however, has to

be provided with a protective layer in order to prevent silicon from penetrating into relatively deep regions. This too is a highly complex and expensive process.

Therefore, the object of the invention is to provide a fibre fiber composite material of the above type which offers an even higher strength and improved pseudoductility of the component. A further object of the invention is to provide a process for producing this material, making the material simple and inexpensive to produce and therefore suitable for series production.

The solution consists in a process having the features of Claim 1 for producing a fiber composite material containing fibers with a high hot strength, based on carbon, silicon, boron and/or nitrogen, which are reaction-bonded to a silicon-based matrix, a pressing compound being produced from fibers, binder and, if appropriate, filler and/or additives, which is then pressed in a press mold to form a green body, wherein various pressing compounds are produced, which contain fibers of different qualities and/or in different proportions, and the press mold is filled with the various pressing compounds in a plurality of successive steps and in a fibre fiber composite material having the features of Claim 16 or 17 containing fibers made by the process. The fibers preferably have a layer of carbon and/or pyrolytic carbon.

The process according to the invention is distinguished by the fact that, to produce the green body, the press is successively filled with the various pressing compounds, the inner pressing compound comprising fibres fibers of a core which is tolerant

to damage, and the outermost pressing compound comprising **fibres fibers** in a ceramicized frictional coating.

5 The material according to the invention is therefore a gradient material, the advantage of which lies in the extremely simple production process according to the invention.

10 According to the invention, during the production of the green body, the pressing compounds, during filling, are to be layered in the press mould mold in such a way that in the final component the frictional layer which has a high wear resistance and is largely ceramicized merges continually into a core which is tolerant to damage. In this way, the high wear 15 resistance is combined with very good mechanical characteristics.

20 Therefore, if the mechanical loads on the component are extremely high, it is possible to further increase strength and extension characteristics, as can be demonstrated for example in the 3-point bending test. Under particularly high mechanical loads, such as for example those caused by high vehicle masses or extreme speeds, it is possible to adapt known processes 25 for the low-cost production of **fibre fiber**-reinforced composite ceramic in such a way that the material or the component offers a high strength and a very good resistance to wear on the outside, combined with a significantly increased pseudoductility on the inside.

30 The advantage of the process according to the invention is that there is no need to join layers with different properties using complex joining processes. In this case, the gradient is produced solely by the

way in which the mould mold is filled. Due to the process used, the individual layers do not have any defined interlayers.

5 The filling heights required can be determined according to the particular application using tests on the compressibility of the various pressing compounds at constant pressure.

~~Advantageous refinements are given in the subclaims.~~

10 A highly ceramicized frictional layer on the component surface, for example the brake disc surface, is obtained by providing the **fibres fibers** which have been processed in the pressing compound with coatings which make it possible for not only carbon-containing fillers and **pyrolysed pyrolyzed** binders but also carbon
15 **fibres fibers** to be partially converted by the molten silicon to form silicon carbide. This is achieved by applying known coatings in a suitably small thickness or using more reactive carbon-containing coatings.

20 As a result, the **fibres fibers** which have been provided with a corresponding thin coating are relatively soft during processing to form the pressing compound. After mixing and pressing, they exhibit a high degree of interlacing. This means there are few, if any, spaces between them in which, for example, silicon can accumulate and therefore remain as unreacted residual silicon following the infiltration with liquid silicon. Furthermore, the **fibres fibers** are reaction-bonded to the matrix. The result is a high proportion of ceramic **fibres fibers**. The
25 frictional layer formed therefore has a high strength with an excellent tolerance to damage and is characterized by a high resistance to wear. A brake
30

disc produced using this process has, for example, a high coefficient of friction with suitably adapted linings.

5 A layer of pyrolytic carbon (PyC) is applied to at least some of the reinforcement fibres fibers used. Only then is a simple dip coating in accordance with the known process carried out.

10 These preferred reinforcement fibres fibers are therefore each individually coated with two additional layers. The bottom layer, which is applied direct to the fibre fiber, is made from pyrolytic carbon. A dip-coating which is known per se comprising a ~~pyrolysable~~ ~~pyrolyzable~~ binder is applied to this layer. During the infiltration of the porous shaped body with liquid silicon, the layer of carbon resulting from the resin coating acts as a "sacrificial layer". The liquid silicon reacts with this outer layer to form silicon carbide. This forms a diffusion barrier to the liquid silicon, which therefore cannot penetrate further into the fibre fiber. The deeper layer of pyrolytic carbon and the reinforcement fibres fibers in the core are not attacked.

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25 The fibres fibers which have been treated in this way are distinguished by a particularly high strength. The additional layer of pyrolytic carbon also produces optimum bonding of the reinforcement fibres fibers to the matrix. They have a crack-diverting action and can slide in the longitudinal direction, resulting in the good results of the strength and 3-point bending tests.
30 fibre fiber-pullout effects are possible.

By using these reinforcement fibres fibers during the production of the fibre fiber composite material

according to the invention, even in small proportions
of the total fibre fiber volume, it is possible to
significantly increase the strength and extension
figures, as can be demonstrated, for example, using the
5 3-point bending test. They do not impair the other
parameters.

By coating the PyC fibres fibers with a resin
solution, it is possible to use these fibres fibers
even for silicized materials.

10 The process for producing these reinforcement
fibres fibers is distinguished by the fact that carbon
fibres fibers are firstly coated with pyrolytic carbon.
This term is understood to mean both pyrolysed
15 pyrolyzed dip coatings, such as for example pitch, and
layers deposited from the vapour vapor phase. The
fibres fibers are then provided with pyrolysable
pyrolyzable plastic material.

20 The coating with pyrolytic carbon may, on the one
hand, be carried out by dip coating, for example by
dipping into a pitch bath. This process is suitable in
particular for long fibres fibers. Alternatively, a
CVD coating, for example using methane in a reactor,
may be applied to the fibres fibers. This process is
eminently suitable for both long fibres fibers and
25 short fibres fibers.

30 The use of pitch has the advantage that the
pyrolytic carbon layer formed is crystalline carbon
which reacts with liquid silicon significantly more
slowly than a layer of amorphous carbon, as is formed,
for example, when a phenolic resin is used. As a
result, the diffusion barrier for the amorphous carbon
is strengthened further.

Long **fibres fibers** are preferably cut after the coating and before they are processed to form a green body.

It is possible to use treated individual **fibres fibers** or fibre fiber bundles. The fibre fiber bundles preferably comprise approximately 1000 to 14,000 individual **fibres fibers**, with mean diameters of approximately 5 to 10 μm and a length of approximately 1 to 30 mm. In this way, it is also possible to use commercially available fibre fiber bundles, allowing inexpensive production.

For the gradient material according to the invention, this means that the pressing compounds which have been layered successively into the press mould mold contain reinforcement **fibres fibers** in which the quality of the fibre fiber coating increases from the outside inwards. For example, in the core of a subsequent brake disc PyC-coated carbon **fibres fibers** are used, so that the entire component is made tolerant to damage. Further filling is with pressing compounds which contain **fibres fibers** of decreasing coating quality, until ultimately **fibres fibers** with only a slight coating – and in extreme cases even uncoated **fibres fibers** – are used for the frictional layer. The outermost layer, which then serves as the actual frictional layer, may therefore comprise predominantly or even entirely silicon carbide, since the slightly coated or even uncoated **fibres fibers** are predominantly or completely converted into silicon carbide during the liquid silicization.

Furthermore, it is possible to achieve the gradient in mechanical and tribological properties not only by using the fibre fiber coating but also by

varying both the fibre fiber quality and the fibre fiber length.

The use of short fibres fibers has the further advantage that the filling and pressing operation also orients fibres fibers perpendicular to the pressing plane, thus ensuring an a continuous transition of the properties.

All customary reinforcement fibres fibers can be used to produce the material according to the invention. Carbon fibres fibers are preferred.

However, other fibres fibers with high hot strength, such as silicon carbide fibres fibers or fibres fibers based on Si/C/B/N, are suitable in principle.

Furthermore, glass fibres fibers or metal fibres fibers, for example fibres fibers based on titanium, are suitable. Aramid fibres fibers are also eminently suitable.

These different variables, in combination, make it possible to produce a defined change in the materials' properties over the thickness of the disc.

Exemplary embodiments of the present invention are described in more detail below with reference to the appended drawings, in which:

Figure 1 shows is a diagrammatic depiction of a cross section through a PyC-coated carbon fibre fiber;

Figure 2 shows is a diagrammatic cross section through a gradient material according to the invention;

Figure 3 is a picture of a brake disc which has been produced using the process according to the invention, in the CRP state (green body); and

Figures 4,5 show 4 and 5 are microsections through the gradient structure of the brake disc shown in Figure 3.

The reinforcement fibre fiber 1 shown in Figure 1 has an inner core 2 made from a carbon fibre fiber. This core 2 is provided with a coating 3 of pyrolytic carbon. The coating 3 is preferably approximately 100-300 nm thick. An outer layer 4 made from a pyrolysable pyrolyzable binder is preferably applied to the coating 3. The layer 4 is preferably approximately 200-800 nm thick. This binder is, for example, a pyrolysable pyrolyzable resin or resin mixture, preferably selected from the group of phenolic resins. The layer 4 is converted into carbon during the subsequent pyrolysis, and this carbon in turn reacts to form silicon carbide during the infiltration with liquid silicon. The inner region of the reinforcement fibre fiber 1, namely the coating 3 of pyrolytic carbon and the core 2 of the reinforcement fibre fiber 1, which is enclosed by the coating 3, are not affected by the liquid silicon.

These fibres fibers can be produced in various ways. One possible process is eminently suitable for coating long fibres fibers. The long fibres fibers are firstly dipped into a pitch bath and are then dried in a drying station. The fibres fibers which have been coated in this way are finally dipped into a bath containing a pyrolysable pyrolyzable phenolic resin. After they have passed through a further drying station, the long fibres fibers are ready for use and may, for example be cut to the desired length.

5 A further possible process is suitable both for coating short fibres fibers and for coating long fibres fibers. The fibres fibers are firstly subjected to a CVD coating, for example using methane, and then to a dip coating in a bath containing ~~pyrolysable~~
pyrolyzable phenolic resin.

10 The production process for the material according to the invention is known per se and is described, for example, in German Patent Application 197 11 829.1.

15 The mixture for producing the green bodies comprises fibres fibers or fibre fiber bundles, a pyrolysable pyrolyzable binder, e.g. a phenolic resin, and, if appropriate, carbon-containing fillers, such as graphite or soot, as well as further fillers, such as silicon, carbides, nitrides or borides, preferably silicon carbide, titanium carbide or titanium boride in powder form. Examples of further preferred fillers for influencing the pyrolysis kinetics, in particular for accelerating the pyrolysis, are polyvinyl alcohol or methylcellulose. Furthermore, additions of iron, chromium, titanium, molybdenum, nickel or aluminium
20 aluminum may be added to the mixture. These additions improve the behaviour behavior of the liquid silicon during the infiltration.

25 The baths may also already contain fillers, such as for example graphite.

30 The carbon-containing fillers assist with cohesion during production and subsequent pyrolysis of the green body and accelerate the pyrolysis. The further fillers are used to adjust the wear resistance of the subsequent composite ceramic.

5 The green body may be produced by dry or hot extrusion of granules. The granules may be obtained by pelletizing the components listed above. Following their production, the granules are dried and pressed to form a green body. It is possible to produce the green body near net shape. Since there is little shrinkage during the pyrolysis and infiltration with liquid silicon, remachining costs are low.

10 However, the mixture described above may also be mixed with heat-curable binders in a kneader, pressed in a mould mold and heat-cured to form a green body. In this case, the green body or the porous shaped body resulting from the pyrolysis of the green body may be machined further to a desired shape.

15 The porosity of the shaped body can be set by selecting the additives and the amount thereof.

Exemplary Embodiment 1

20 Three different pressing compounds were produced from short fibres fibers SCF6 with a length of 6 mm and short fibres fibers SCF3 with a length of 3 mm, produced by SGL, phenolic resin, titanium carbide and graphite filler.

25 Pressing compound 1 contained 3 mm fibres fibers with exclusively a commercially available epoxy resin coat. Pressing compound 2 contained 6 mm fibres fibers which were coated by impregnation in a pitch solution (Carbores, produced by Rüttgers) and subsequent drying. The coated fibres fibers were then impregnated by immersion in a highly dilute phenolic resin solution and subsequent drying in a circulating-air cabinet at 30 130°C. Pressing compound 3 contained a mixture of 3 mm

5 and 6 mm ~~fibres~~ fibers in a ratio of 1:2, which, as described above, were firstly dipped into the pitch solution referred to above and then into a concentrated phenolic resin solution. This was again followed by a drying and curing step.

10 The three pressing compounds were produced from the different coated ~~fibres~~ fibers using a known process. To do this, untreated or treated ~~fibres~~ fibers were mixed with phenolic resin, titanium carbide and graphite as filler in a mixing kneader to form a pressing compound. The ~~fibres~~ fibers formed 38% by volume.

15 These pressing compounds were used to produce a brake disc. To do this, the near net shape ~~mould~~ mold of a hot press was filled. The filling took place in five steps without preforming. Firstly, the ~~mould~~ mold was filled with pressing compound 1; the height of the layer was approx. 13 mm. This was followed by a second layer of pressing compound 2, to a height of approximately 10 mm, a third layer of pressing compound 3, to a height of approximately 20 mm, a fourth layer of pressing compound 2, to a height of approximately 10 mm, and a fifth and final layer of pressing compound 1, to a height of approximately 13 mm. These layers were 20 pressed under a pressure of approximately 80 bar. The result was a disc with a thickness of approximately 25 mm.

25 This pressing compound was cured at approximately 150°C to form a dimensionally stable CRP disc, as shown 30 in Figure 3. Pyrolysis took place at 800°C in a pyrolysis furnace under inert gas. The subsequent infiltration with liquid silicon was carried out in ~~vaccuo~~ vacuo at approximately 1600°C, using molten

silicon. The resultant C/SiC body was cooled to room temperature.

The resultant brake disc was tested with brake linings made from the same material with a lower silicon content. The coefficients of friction were very good at 0.55 - 0.6.

The flexural strengths were determined separately for the individual layers. The 3-point bending strength of the material derived from the pressing compound 1 was approximately 170 MPa with an extension of 0.12%. The 3-point bending strength of the material derived from pressing compound 2 was approximately 91 MPa with an extension of 0.09%. Finally, the 3-point bending strength of the material derived from pressing compound 3 was approximately 67 MPa with an extension of 0.21%.

Exemplary Embodiment 2

The same proportions of short fibres fibers SCF3 with a length of 3 mm and short fibres fibers SCF6 with a length of 6 mm produced by SGL and T 800/6K fibres fibers produced by Toray with a length of 24 mm were used. The 3 mm fibres fibers and 6 mm fibres fibers were firstly provided, as described above, with a layer of pyrolytic carbon and then with a layer of phenolic resin. The 24 mm fibres fibers had a layer of pyrolytic carbon (PyC) applied using a CVD process by means of methane, and a resin coating which was applied by dipping.

The fibres fibers which had been treated in this way were processed to form a pressing compound as described above. The fibres fibers which had been

coated according to the invention again constituted 38%. These ~~fibres~~ **fibers** were mixed with phenolic resin, titanium carbide and graphite as filler, in a mixing kneader, to form a pressing compound.

5 Three different pressing compounds were produced, as described above, with pressing compounds 1 and 2 having the compositions described above and pressing compound 3 containing a mixture of 24 mm ~~fibres~~ **fibers** and 6 mm ~~fibres~~ **fibers**, in a ratio of 1:2.

10 The near net shape ~~mould~~ **mold** of the hot press was filled in five steps without preforming, as described above, the filling height of the layers of the pressing compound 1 being in each case 10 mm, and the height of the layers of the pressing compound 2 in each case being approximately 12 mm. The layered arrangement was pressed at 80 bar. The result was a disc with a thickness of approx. 25 mm.

15 The pressing compound was cured at approximately 150°C to form a dimensionally stable CRP disc.

20 Pyrolysis took place at 800°C in a pyrolysis furnace under inert gas. The subsequent silicization was carried out in vacuo at approximately 1600°C using molten silicon. The resultant C/SiC body was cooled to room temperature.

25 The coefficients of friction, which were measured as described above, were once again 0.55 - 0.6. The 3-point bending strength of the material derived from pressing compound 2 (thick resin coating) was approx. 67 MPa with an extension of 0.21%. The 3-point bending strength of material derived from pressing compound 3 (PyC-resin coating) was approximately 107 MPa with an extension of 0.42%.

Figure 2 diagrammatically depicts a cross section through a brake disc 10 produced using this process. The central opening in the brake disc is denoted by 11, and the disc material itself is denoted by 12. The
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brake disc 10 comprises the gradient material 12 according to the invention. The outermost regions 13a, 13b at the surface of the brake disc 10 form the frictional surfaces. They comprise wear-resistant, high-strength ceramic substance. The central region 15
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in the interior of the brake disc 10 forms a core which is tolerant to damage. It comprises a carbon-containing material with relatively unpronounced ceramic properties, lacking in particular the brittleness which is typical of ceramic materials. The regions 14a and 14b form intermediate regions, the material of which is not as strongly ceramic as that of the outer regions 13a, 13b but also not as carbonaceous as the material of the central region 15.

The phase boundaries 16a, b, c, and d between the individual regions 13a, b, 14a, b, 15 are not sharply emphasized, but rather are more gradual. Preferably, they merge into one another. The process according to the invention ensures a gradual transition and therefore good cohesion between the regions.

25 Additional joining processes are not required.

Figure 3 shows a brake disc which has been produced in accordance with Exemplary Embodiment 1 in the CRP state i.e. after pressing but before
30 ~~pyrolysis~~ pyrolysis of the green body and before infiltration with liquid silicon.

Figures 4 and 5 show microsections through the gradient structure of the porous shaped body shown in

Figures 2 and 3. The various layers which merge
seamlessly into one another can be seen clearly.

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5 Process for producing a fibre composite material

The invention relates to a process for producing a fibre composite material according the preamble of Claim 1 and to a fibre composite material according the 10 preamble of Claim 16 or 17.

A process of the generic type and a ceramic composite material of the generic type are described in German Patent Application 197 11 829.1, which is not a prior 15 publication. The reinforcing fibres which are known from this document are fibres with a high hot strength which are present in the form of short fibre bundles. The fibre bundles are impregnated with a binder which is suitable for pyrolysis. For this purpose, the fibre 20 bundles are dipped into the binder. The binder is then solidified. Consequently, the fibre bundles are held together and mechanically reinforced. The fibre bundles are mixed with further binders and fillers and the mixture is hot-pressed to form a CRP body or "green 25 body", which is then pyrolysed in vacuo or under an inert gas to form a shaped body with a carbon matrix (C/C body). In the process, the fibre coating is also converted so that the fibre bundles are then coated with a layer of carbon. The shaped body is then 30 infiltrated with molten silicon. The result is a C/SiC fibre composite material in which the fibre bundles are embedded in a matrix based on SiC. The short fibre bundles are embedded in the matrix in a randomly distributed form, with the individual filaments being 35 substantially maintained. The carbon coating has reacted with the matrix material. As a result, the fibre bundles are protected from the aggressive attack from the molten silicon. This fibre composite ceramic

exhibits very good tribological properties and, furthermore, is relatively inexpensive and easy to produce. It is suitable in particular for the production of brake discs and/or brake linings.

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However, this material is unable to withstand particularly high mechanical loads, such as for example those which are generated by high vehicle masses or extreme speeds, since it is too brittle and 10 insufficiently tolerant to damage to do so.

Various solutions have already been proposed in order to circumvent this problem. German Utility Model 296 10 498 describes a vehicle brake disc or vehicle 15 clutch disc made from C-C/SiC composite material in which the disc has an SiC coating. Therefore, the outer region of the disc is made from ceramic material and provides very good frictional characteristics, while the core is a carbon body which, due to its 20 pseudoductility, has high tolerance to damage. However, bodies that are coated in this way are complex and therefore expensive to produce. For this reason, they are only used for special applications, for example in motor racing.

25

European Patent Application EP 0 564 245 likewise describes a multilayer material which, however, has to be provided with a protective layer in order to prevent silicon from penetrating into relatively deep regions. 30 This too is a highly complex and expensive process.

Therefore, the object of the invention is to provide a fibre composite material of the above type which offers an even higher strength and improved pseudoductility of 35 the component. A further object of the invention is to provide a process for producing this material, making the material simple and inexpensive to produce and therefore suitable for series production.

The solution consists in a process having the features of Claim 1 and in a fibre composite material having the features of Claim 16 or 17.

- 5 The process according to the invention is distinguished by the fact that, to produce the green body, the press is successively filled with the various pressing compounds, the inner pressing compound comprising fibres of a core which is tolerant to damage, and the
10 outermost pressing compound comprising fibres in a ceramicized frictional coating.

The material according to the invention is therefore a gradient material, the advantage of which lies in the
15 extremely simple production process according to the invention.

According to the invention, during the production of the green body, the pressing compounds, during filling,
20 are to be layered in the press mould in such a way that in the final component the frictional layer which has a high wear resistance and is largely ceramicized merges continually into a core which is tolerant to damage. In this way, the high wear resistance is combined with
25 very good mechanical characteristics.

Therefore, if the mechanical loads on the component are extremely high, it is possible to further increase strength and extension characteristics, as can be
30 demonstrated for example in the 3-point bending test. Under particularly high mechanical loads, such as for example those caused by high vehicle masses or extreme speeds, it is possible to adapt known processes for the low-cost production of fibre-reinforced composite
35 ceramic in such a way that the material or the component offers a high strength and a very good resistance to wear on the outside, combined with a significantly increased pseudoductility on the inside.

The advantage of the process according to the invention is that there is no need to join layers with different properties using complex joining processes. In this case, the gradient is produced solely by the way in
5 which the mould is filled. Due to the process used, the individual layers do not have any defined interlayers.

The filling heights required can be determined according to the particular application using tests on
10 the compressibility of the various pressing compounds at constant pressure.

Advantageous refinements are given in the subclaims.

15 A highly ceramicized frictional layer on the component surface, for example the brake disc surface, is obtained by providing the fibres which have been processed in the pressing compound with coatings which make it possible for not only carbon-containing fillers and pyrolysed binders but also carbon fibres to be partially converted by the molten silicon to form silicon carbide. This is achieved by applying known coatings in a suitably small thickness or using more reactive carbon-containing coatings.
25

As a result, the fibres which have been provided with a corresponding thin coating are relatively soft during processing to form the pressing compound. After mixing and pressing, they exhibit a high degree of
30 interlacing. This means there are few, if any, spaces between them in which, for example, silicon can accumulate and therefore remain as unreacted residual silicon following the infiltration with liquid silicon. Furthermore, the fibres are reaction-bonded to the
35 matrix. The result is a high proportion of ceramic fibres. The frictional layer formed therefore has a high strength with an excellent tolerance to damage and is characterized by a high resistance to wear. A brake disc produced using this process has, for example, a

high coefficient of friction with suitably adapted linings.

A layer of pyrolytic carbon (PyC) is applied to at 5 least some of the reinforcement fibres used. Only then is a simple dip coating in accordance with the known process carried out.

These preferred reinforcement fibres are therefore each 10 individually coated with two additional layers. The bottom layer, which is applied direct to the fibre, is made from pyrolytic carbon. A dip-coating which is known per se comprising a pyrolysable binder is applied to this layer. During the infiltration of the porous 15 shaped body with liquid silicon, the layer of carbon resulting from the resin coating acts as a "sacrificial layer". The liquid silicon reacts with this outer layer to form silicon carbide. This forms a diffusion barrier to the liquid silicon, which therefore cannot penetrate 20 further into the fibre. The deeper layer of pyrolytic carbon and the reinforcement fibres in the core are not attacked.

The fibres which have been treated in this way are 25 distinguished by a particularly high strength. The additional layer of pyrolytic carbon also produces optimum bonding of the reinforcement fibres to the matrix. They have a crack-diverting action and can slide in the longitudinal direction, resulting in the 30 good results of the strength and 3-point bending tests. Fibre-pullout effects are possible.

By using these reinforcement fibres during the production of the fibre composite material according to 35 the invention, even in small proportions of the total fibre volume, it is possible to significantly increase the strength and extension figures, as can be demonstrated, for example, using the 3-point bending test. They do not impair the other parameters.

By coating the PyC fibres with a resin solution, it is possible to use these fibres even for silicized materials.

5

The process for producing these reinforcement fibres is distinguished by the fact that carbon fibres are firstly coated with pyrolytic carbon. This term is understood to mean both pyrolysed dip coatings, such 10 as for example pitch, and layers deposited from the vapour phase. The fibres are then provided with pyrolysable plastic material.

15 The coating with pyrolytic carbon may, on the one hand, be carried out by dip coating, for example by dipping into a pitch bath. This process is suitable in particular for long fibres. Alternatively, a CVD coating, for example using methane in a reactor, may be applied to the fibres. This process is eminently 20 suitable for both long fibres and short fibres.

25 The use of pitch has the advantage that the pyrolytic carbon layer formed is crystalline carbon which reacts with liquid silicon significantly more slowly than a layer of amorphous carbon, as is formed, for example, when a phenolic resin is used. As a result, the diffusion barrier for the amorphous carbon is strengthened further.

30 Long fibres are preferably cut after the coating and before they are processed to form a green body.

35 It is possible to use treated individual fibres or fibre bundles. The fibre bundles preferably comprise approximately 1000 to 14,000 individual fibres, with mean diameters of approximately 5 to 10 μm and a length of approximately 1 to 30 mm. In this way, it is also possible to use commercially available fibre bundles, allowing inexpensive production.

For the gradient material according to the invention, this means that the pressing compounds which have been layered successively into the press mould contain
5 reinforcement fibres in which the quality of the fibre coating increases from the outside inwards. For example, in the core of a subsequent brake disc PyC-coated carbon fibres are used, so that the entire component is made tolerant to damage. Further filling
10 is with pressing compounds which contain fibres of decreasing coating quality, until ultimately fibres with only a slight coating - and in extreme cases even uncoated fibres - are used for the frictional layer. The outermost layer, which then serves as the actual
15 frictional layer, may therefore comprise predominantly or even entirely silicon carbide, since the slightly coated or even uncoated fibres are predominantly or completely converted into silicon carbide during the liquid silicization.

20

Furthermore, it is possible to achieve the gradient in mechanical and tribological properties not only by using the fibre coating but also by varying both the fibre quality and the fibre length.

25

The use of short fibres has the further advantage that the filling and pressing operation also orients fibres perpendicular to the pressing plane, thus ensuring an continuous transition of the properties.

30

All customary reinforcement fibres can be used to produce the material according to the invention. Carbon fibres are preferred. However, other fibres with high hot strength, such as silicon carbide fibres or fibres
35 based on Si/C/B/N, are suitable in principle. Furthermore, glass fibres or metal fibres, for example fibres based on titanium, are suitable. Aramid fibres are also eminently suitable.

These different variables, in combination, make it possible to produce a defined change in the materials' properties over the thickness of the disc.

- 5 Exemplary embodiments of the present invention are described in more detail below with reference to the appended drawings, in which:

Figure 1 shows a diagrammatic depiction of a
10 cross section through a PyC-coated carbon fibre;

Figure 2 shows a diagrammatic cross section through a gradient material according to
15 the invention;

Figure 3 a picture of a brake disc which has been produced using the process according to
20 the invention, in the CRP state (green body);

Figures 4,5 show microsections through the gradient structure of the brake disc shown in Figure 3.

25 The reinforcement fibre 1 shown in Figure 1 has an inner core 2 made from a carbon fibre. This core 2 is provided with a coating 3 of pyrolytic carbon. The coating 3 is preferably approximately 100-300 nm thick.

30 An outer layer 4 made from a pyrolysable binder is preferably applied to the coating 3. The layer 4 is preferably approximately 200-800 nm thick. This binder is, for example, a pyrolysable resin or resin mixture, preferably selected from the group of phenolic resins.

35 The layer 4 is converted into carbon during the subsequent pyrolysis, and this carbon in turn reacts to form silicon carbide during the infiltration with liquid silicon. The inner region of the reinforcement fibre 1, namely the coating 3 of pyrolytic carbon and

the core 2 of the reinforcement fibre 1, which is enclosed by the coating 3, are not affected by the liquid silicon.

- 5 These fibres can be produced in various ways. One possible process is eminently suitable for coating long fibres. The long fibres are firstly dipped into a pitch bath and are then dried in a drying station. The fibres which have been coated in this way are finally dipped
10 into a bath containing a pyrolysable phenolic resin. After they have passed through a further drying station, the long fibres are ready for use and may, for example be cut to the desired length.
- 15 A further possible process is suitable both for coating short fibres and for coating long fibres. The fibres are firstly subjected to a CVD coating, for example using methane, and then to a dip coating in a bath containing pyrolysable phenolic resin.
20 The production process for the material according to the invention is known per se and is described, for example, in German Patent Application 197 11 829.1.
- 25 The mixture for producing the green bodies comprises fibres or fibre bundles, a pyrolysable binder, e.g. a phenolic resin, and, if appropriate, carbon-containing fillers, such as graphite or soot, as well as further fillers, such as silicon, carbides, nitrides or
30 borides, preferably silicon carbide, titanium carbide or titanium boride in powder form. Examples of further preferred fillers for influencing the pyrolysis kinetics, in particular for accelerating the pyrolysis, are polyvinyl alcohol or methylcellulose. Furthermore,
35 additions of iron, chromium, titanium, molybdenum, nickel or aluminium may be added to the mixture. These additions improve the behaviour of the liquid silicon during the infiltration.

The baths may also already contain fillers, such as for example graphite.

5 The carbon-containing fillers assist with cohesion during production and subsequent pyrolysis of the green body and accelerate the pyrolysis. The further fillers are used to adjust the wear resistance of the subsequent composite ceramic.

10 The green body may be produced by dry or hot extrusion of granules. The granules may be obtained by pelletizing the components listed above. Following their production, the granules are dried and pressed to form a green body. It is possible to produce the green body near net shape. Since there is little shrinkage 15 during the pyrolysis and infiltration with liquid silicon, remachining costs are low.

20 However, the mixture described above may also be mixed with heat-curable binders in a kneader, pressed in a mould and heat-cured to form a green body. In this case, the green body or the porous shaped body resulting from the pyrolysis of the green body may be machined further to a desired shape.

25 The porosity of the shaped body can be set by selecting the additives and the amount thereof.

Exemplary Embodiment 1

30 Three different pressing compounds were produced from short fibres SCF6 with a length of 6 mm and short fibres SCF3 with a length of 3 mm, produced by SGL, phenolic resin, titanium carbide and graphite filler.

35 Pressing compound 1 contained 3 mm fibres with exclusively a commercially available epoxy resin coat. Pressing compound 2 contained 6 mm fibres which were coated by impregnation in a pitch solution (Carbores,

produced by Rüttgers) and subsequent drying. The coated fibres were then impregnated by immersion in a highly dilute phenolic resin solution and subsequent drying in a circulating-air cabinet at 130°C. Pressing compound 3
5 contained a mixture of 3 mm and 6 mm fibres in a ratio of 1:2, which, as described above, were firstly dipped into the pitch solution referred to above and then into a concentrated phenolic resin solution. This was again followed by a drying and curing step.

10

The three pressing compounds were produced from the different coated fibres using a known process. To do this, untreated or treated fibres were mixed with phenolic resin, titanium carbide and graphite as filler
15 in a mixing kneader to form a pressing compound. The fibres formed 38% by volume.

20

These pressing compounds were used to produce a brake disc. To do this, the near net shape mould of a hot press was filled. The filling took place in five steps without preforming. Firstly, the mould was filled with pressing compound 1; the height of the layer was approx. 13 mm. This was followed by a second layer of pressing compound 2, to a height of approximately 10 mm, a third layer of pressing compound 3, to a height of approximately 20 mm, a fourth layer of pressing compound 2, to a height of approximately 10 mm, and a fifth and final layer of pressing compound 1, to a height of approximately 13 mm. These layers were
25 pressed under a pressure of approximately 80 bar. The result was a disc with a thickness of approximately 30 25 mm.

35

This pressing compound was cured at approximately 150°C to form a dimensionally stable CRP disc, as shown in Figure 3. Pyrolysis took place at 800°C in a pyrolysis furnace under inert gas. The subsequent infiltration with liquid silicon was carried out in vaccuo at

approximately 1600°C, using molten silicon. The resultant C/SiC body was cooled to room temperature.

5 The resultant brake disc was tested with brake linings made from the same material with a lower silicon content. The coefficients of friction were very good at 0.55 - 0.6.

10 The flexural strengths were determined separately for the individual layers. The 3-point bending strength of the material derived from the pressing compound 1 was approximately 170 MPa with an extension of 0.12%. The 3-point bending strength of the material derived from pressing compound 2 was approximately 91 MPa with an 15 extension of 0.09%. Finally, the 3-point bending strength of the material derived from pressing compound 3 was approximately 67 MPa with an extension of 0.21%.

20 Exemplary Embodiment 2

25 The same proportions of short fibres SCF3 with a length of 3 mm and short fibres SCF6 with a length of 6 mm produced by SGL and T 800/6K fibres produced by Toray with a length of 24 mm were used. The 3 mm fibres and 6 mm fibres were firstly provided, as described above, with a layer of pyrolytic carbon and then with a layer of phenolic resin. The 24 mm fibres had a layer of 30 pyrolytic carbon (PyC) applied using a CVD process by means of methane, and a resin coating which was applied by dipping.

35 The fibres which had been treated in this way were processed to form a pressing compound as described above. The fibres which had been coated according to the invention again constituted 38%. These fibres were mixed with phenolic resin, titanium carbide and graphite as filler, in a mixing kneader, to form a pressing compound.

Three different pressing compounds were produced, as described above, with pressing compounds 1 and 2 having the compositions described above and pressing compound 3 containing a mixture of 24 mm fibres and 6 mm fibres,
5 in a ratio of 1:2.

The near net shape mould of the hot press was filled in five steps without preforming, as described above, the filling height of the layers of the pressing compound 1
10 being in each case 10 mm, and the height of the layers of the pressing compound 2 in each case being approximately 12 mm. The layered arrangement was pressed at 80 bar. The result was a disc with a thickness of approx. 25 mm.
15

The pressing compound was cured at approximately 150°C to form a dimensionally stable CRP disc. Pyrolysis took place at 800°C in a pyrolysis furnace under inert gas. The subsequent silicization was carried out in vacuo at
20 approximately 1600°C using molten silicon. The resultant C/SiC body was cooled to room temperature.

The coefficients of friction, which were measured as described above, were once again 0.55 - 0.6. The 3-point bending strength of the material derived from
25 pressing compound 2 (thick resin coating) was approx. 67 MPa with an extension of 0.21%. The 3-point bending strength of material derived from pressing compound 3 (PyC-resin coating) was approximately 107 MPa with an extension of 0.42%.
30

Figure 2 diagrammatically depicts a cross section through a brake disc 10 produced using this process. The central opening in the brake disc is denoted by 11,
35 and the disc material itself is denoted by 12. The brake disc 10 comprises the gradient material 12 according to the invention. The outermost regions 13a, 13b at the surface of the brake disc 10 form the frictional surfaces. They comprise wear-resistant,

high-strength ceramic substance. The central region 15 in the interior of the brake disc 10 forms a core which is tolerant to damage. It comprises a carbon-containing material with relatively unpronounced ceramic properties, lacking in particular the brittleness which is typical of ceramic materials. The regions 14a and 14b form intermediate regions, the material of which is not as strongly ceramic as that of the outer regions 13a, 13b but also not as carbonaceous as the material of the central region 15.

The phase boundaries 16a, b, c, and d between the individual regions 13a, b, 14a, b, 15 are not sharply emphasized, but rather are more gradual. Preferably, they merge into one another. The process according to the invention ensures a gradual transition and therefore good cohesion between the regions. Additional joining processes are not required.

Figure 3 shows a brake disc which has been produced in accordance with Exemplary Embodiment 1 in the CRP state i.e. after pressing but before pyrolysis of the green body and before infiltration with liquid silicon.

Figures 4 and 5 show microsections through the gradient structure of the porous shaped body shown in Figures 2 and 3. The various layers which merge seamlessly into one another can be seen clearly.

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PCT/EP99/00611

DaimlerChrysler AG
Stuttgart

FTP/P ibr-mw
08.02.2000

New Patent Claims

1. Process for producing a fibre composite material containing fibres with a high hot strength, based on carbon, silicon, boron and/or nitrogen, which are reaction-bonded to a silicon-based matrix, a pressing compound being produced from fibres, binder and, if appropriate, filler and/or additives, which is then pressed in a press mould to form a green body, characterized in that various pressing compounds are produced, which contain fibres of different qualities and/or in different proportions, and the press mould is filled with the various pressing compounds in a plurality of successive steps.
2. Process according to Claim 1, wherein the press mould is filled without preforming.
3. Process according to one of the preceding claims, characterized in that fibres which have been coated with a layer of pyrolysable binder are used.
4. Process according to one of the preceding claims, characterized in that fibres which have been coated with a layer of pyrolytic carbon and with a layer of pyrolysable binder are used.
5. Process according to one of the preceding claims, characterized in that differently coated fibres are used for the various pressing compounds.
6. Process according to Claim 5, characterized in that the press mould is filled with the differently coated fibres in such a manner that a green body is

formed, from which it is possible to obtain a fibre composite material with a substantially graphite core and a substantially ceramic surface.

7. Process according to Claim 6, characterized in that fibres with a pronounced coating are used for the substantially graphite core and fibres with a thin coating and/or fibres without a coating are used for the substantially ceramic surface.

8. Process according to Claim 6, characterized in that fibres with a coating which is relatively unreactive with respect to the matrix are used for the substantially graphite core and fibres with a coating which is more reactive with respect to the matrix are used for the substantially ceramic surface.

9. Process according to one of the preceding claims, characterized in that substantially short fibres or short fibre bundles are used to produce the pressing compounds.

10. Process according to one of the preceding claims, characterized in that fibres of different lengths are used for the various pressing compounds.

11. Process according to one of the preceding claims, characterized in that fibres made from different materials are used for the various pressing compounds.

12. Process according to one of the preceding claims, characterized in that to produce the pressing compounds the individual components are processed into granules, in particular by being pelletized, and the granules are dried and pressed to form the green body.

13. Process according to Claim 12, characterized in that the granules are pressed by dry or hot extrusion.

14. Process according to one of Claims 1 to 11, characterized in that to produce the pressing compound the individual components are mixed in a kneader and the mixture is pressed to form a green body.
15. Process according to one of the preceding claims, characterized in that a heat-curable binder is added to the pressing compound, and the pressed green body is cured by heating.
16. Fibre composite material containing fibres with a high hot strength, based on carbon, silicon, boron and/or nitrogen, which are reaction-bonded to a silicon-based matrix, characterized in that it can be produced using the process according to one of Claims 1 to 15.
17. Fibre composite material according to Claim 16, characterized in that it contains fibres with a layer of carbon and/or pyrolytic carbon.
18. Fibre composite material according to Claim 16 or 17, characterized in that the various layers have differently coated fibres.
19. Fibre composite material according to one of Claims 16 to 18, characterized in that it has a substantially graphite core and a substantially ceramic surface
20. Fibre composite material according to Claim 19, characterized in that the substantially graphite core contains fibres with a pronounced coating and the substantially ceramic surface contains fibres with a thin coating and/or fibres without a coating.

21. Fibre composite material according to Claim 19, characterized in that the substantially graphite core contains few or no fibres which are reaction-bonded to the matrix, and the substantially ceramic surface contains predominantly or exclusively fibres which are reaction-bonded to the matrix.

22. Fibre composite material according to one of Claims 16 to 21, characterized in that it substantially contains short fibres or short fibre bundles.

23. Fibre composite material according to one of Claims 16 to 22, characterized in that the various layers contain fibres of different lengths.

24. Fibre composite material according to one of Claims 16 to 23, characterized in that the various layers contain fibres made from different materials.

DaimlerChrysler AG
Stuttgart

Abstract

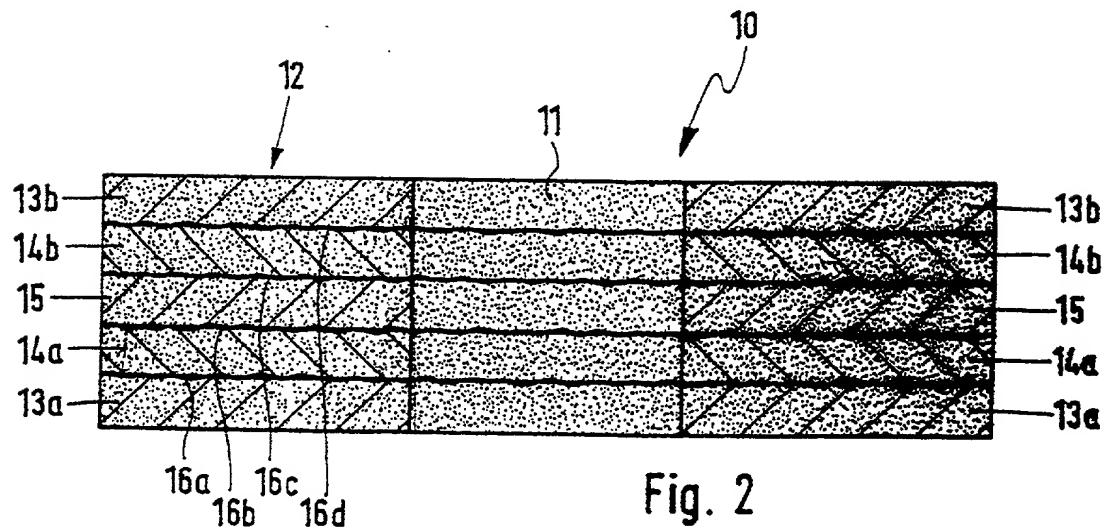
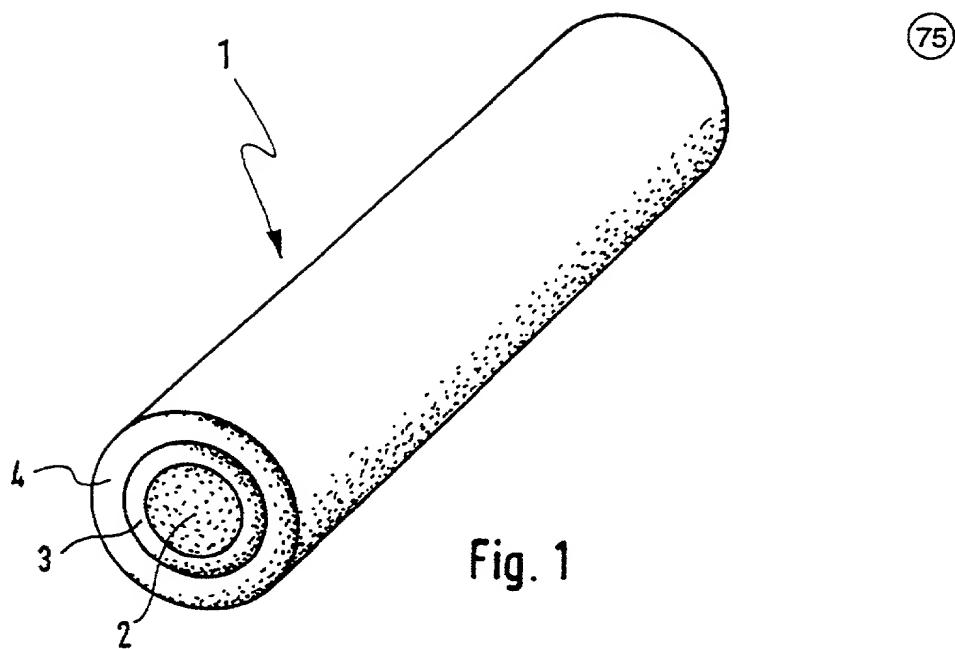
The invention relates to a process for producing a fibre composite material containing fibres with a high hot strength, in particular based on carbon, silicon, boron and/or nitrogen, a pressing compound being produced from fibres, binder and, if appropriate, fillers and/or additives, which is then pressed in a press mould to form a green body. According to the invention, characterized in that various pressing compounds are produced, which contain fibres of different qualities and/or in different proportions, and the press mould is filled with the various pressing compounds in a plurality of successive steps. The invention also relates to a fibre composite material of this nature.

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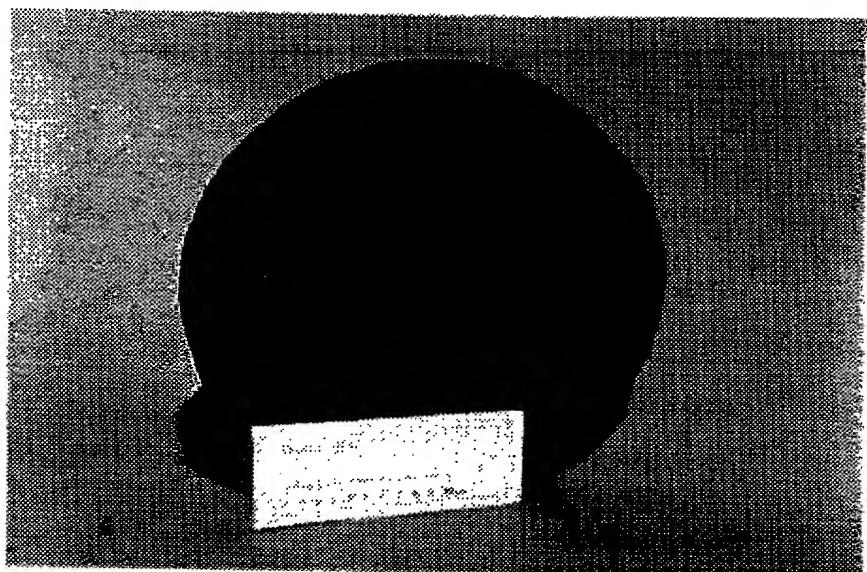
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Figure 3



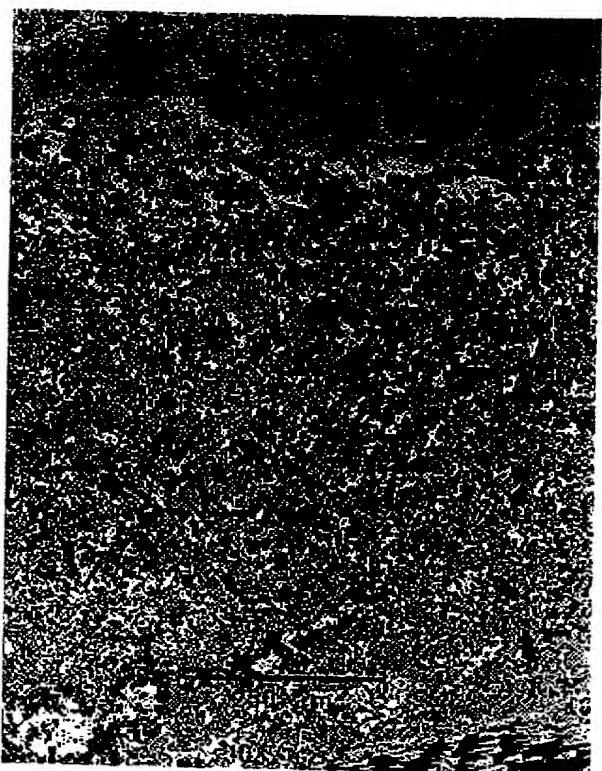
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Figure4



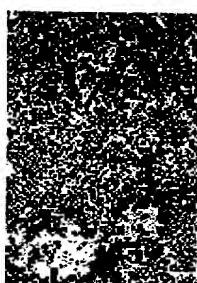
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Figure5



DECLARATION AND POWER OF ATTORNEY - PATENT APPLICATION

As a below named inventor, I hereby declare that my citizenship, postal address and residence are as stated below; that I verily believe I am the original, first and sole inventor (if only one inventor is named below) or a joint inventor (if plural inventors are named below) of the invention entitled:

PROCESS FOR PRODUCING A FIBRE COMPOSITE MATERIAL

the specification of which

 is attached hereto, or

X was filed on January 30, 1999 as International Application No. PCT/EP99/00611.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to be material to patentability as defined in 37 CFR §1.56. I hereby claim foreign priority benefits under Title 35, United States Code §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Claimed

<u>198 05 868.3</u> <u>(Number)</u>	<u>Germany</u> <u>(Country)</u>	<u>13 February 1998</u> <u>(Day/Month/Year)</u>	<u>X</u>
<u> </u> <u>(Number)</u>	<u> </u> <u>(Country)</u>	<u> </u> <u>(Day/Month/Year)</u>	<u> </u>

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose all information known to be material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

<u>(Application Serial No.)</u>	<u>(Filing Date)</u>	<u>(Status)</u>
---------------------------------	----------------------	-----------------

I hereby appoint as principal attorneys Herbert I. Cantor, Reg. No. 24,392; James F. McKeown, Reg. No. 25,406; Donald D. Evenson, Reg. No. 26,160; Joseph D. Evans, Reg. No. 26,269; Gary R. Edwards, Reg. No. 31,824; and Jeffrey D. Sanok, Reg. No. 32,169, to prosecute and transact all business in the Patent and Trademark Office connected with this application and any related United States and international applications. Please direct all communications to:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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Thierry Haug
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PATENT TRADEMARK OFFICE

DECLARATION AND POWER OF ATTORNEY

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Attorney Docket No. 225/49093

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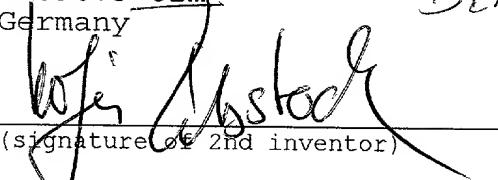
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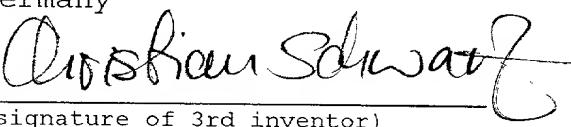
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1st Oct. 2000

(date)


Christian Schwarz
(signature of 3rd inventor)

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